Photochemistry of Dicarbonyldinitrosyliron in Frozen Gas Matrices at 20 K. Infrared Spectroscopic Evidence for Carbonyldinitrosyliron and Carbonyl(dinitrogen)dinitrosyliron

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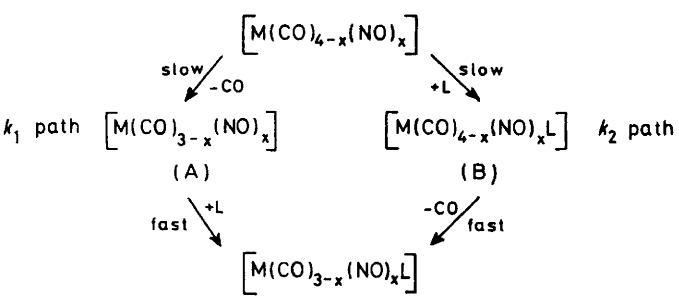
Infrared evidence is presented for the formation of a planar three-co-ordinate species, $[Fe(CO)(NO)_2]$, on u.v. photolysis of $[Fe(CO)_2(NO)_2]$ in argon and methane matrices, and for the formation of four-co-ordinate species, $[Fe(CO)(N_2)(NO)_2]$ and probably $[Fe(N_2)_2(NO)_2]$ in nitrogen matrices at 20 K. The primary photolysis steps are readily reversed by irradiation with visible light. The results are related to the postulate of co-ordinatively unsaturated and expanded-co-ordination-shell species as intermediates in the thermal substitution reactions of $[Fe(CO)_2(NO)_2]$.

THE thermal substitution reactions of the pseudo-$[Ni(CO)_4]$ series of complexes $[M(CO)_{4-x}(NO)_x]$ in solution can be represented mechanistically by Scheme 1 involving two paths, k_1 and k_2, corresponding to the rate-determining step being a dissociative or an associative process respectively. In contrast to the simple behaviour of $[Ni(CO)_4]$, which undergoes substitution and exchange of CO by a dissociative mechanism (k_1 path),[1] the substitution reactions of the mixed carbonyl nitrosyls $[Co(CO)_3(NO)]$ [2,3] and $[Fe(CO)_2(NO)_2]$ [4] follow a two-term rate law (1). 'Poor' ligands, *e.g.* $AsPh_3$, react slowly with $[Co(CO)_3(NO)]$ and $[Fe(CO)_2(NO)_2]$ and the rate is dependent only on the concentration of the nitrosyl complex, which suggests that (A), a co-ordinatively unsaturated species, is a possible intermediate. For 'good' ligands, *e.g.* PPh_3, the contribution from the ligand-independent path (k_1) is negligible so that an expanded-co-ordination-number species (B) is a possible intermediate in this case. The exchange of ^{15}NO with $[Fe(CO)_2(NO)_2]$ takes place [5] by a second-order reaction which also implicates an intermediate of type (B). The availability of the second-order associative mechanism is generally regarded as a consequence of the ability of the co-ordinated NO molecule to accept additional electron density from the metal atom which can thus accommodate the extra ligand (L) and form (B). Both (A) and (B) are likely to be highly reactive so that to detect them, and hence provide direct evidence for the paths proposed, would require either a rapid detection technique, *e.g.* flash photolysis,[6] or a means of stabilising them at low temperatures, *e.g.* the matrix-isolation technique.[7]



SCHEME 1

$$\text{Rate} = (k_1 + k_2[L])[\text{nitrosyl complex}] \qquad (1)$$

Recently we described [8] i.r. evidence for the formation of $[Co(CO)_2(NO)]$, *i.e.* a type (A) species, on the u.v. photolysis of $[Co(CO)_3(NO)]$ in argon and methane matrices at 20 K. In this paper we describe the production of a variety of species formed from $[Fe(CO)_2(NO)_2]$ in inert (argon and methane) and reactive matrices (nitrogen) and we relate the findings to the substitution-reaction studies.[4,5] Preliminary results have been described elsewhere.[9]

EXPERIMENTAL

Details of the cryostat, the i.r. spectrometer, the photolysis lamp, matrix, gases, and the preparation of gas mixtures with substrate : matrix gas ratios of between 1 : 5 000 and 1 : 20 000 have been given previously.[8] Infrared band positions are accurate to better than ±0.5 cm^{-1} but have been rounded to the nearest unit. Dicarbonyldinitrosyliron was prepared by the literature method.[10] Wavelength selection for photolysis was achieved by a combination of absorbing materials: filter A, $\lambda < 280$, $\lambda > 550$ nm [quartz gas cell (pathlength, 25 mm) containing 3 atm of Cl_2 gas + quartz gas cell (pathlength, 25 mm) containing 200 Torr of Br_2 gas]; ‡ filter B, $\lambda > 400$ mm [quartz gas cell containing Cl_2 gas + soda glass disc (thickness, 5 mm)]; filter C, $330 < \lambda < 450$ nm [solution cell (pathlength, 10 mm) containing AnalaR $Co[SO_4]$ in water + solution cell (pathlength, 10 mm) containing AnalaR $Cu[SO_4]$ in water with dilution-adjusted cut-on and cut-off points]; filter D, $230 < \lambda < 280$ nm [quartz gas cell containing Cl_2 gas + quartz solution cells (pathlength, 10 mm) containing AnalaR $Co[SO_4]$ in water

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‡ Throughout this paper: 1 atm = 101 325 Pa; 1 Torr = (101 325/760) Pa.

[1] J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1968, **90**, 6927.

[2] E. M. Thorsteinson and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 3929.

[3] G. Cardaci, A. Foffani, G. Distefano, and G. Innorta, *Inorg. Chim. Acta*, 1962, **1**, 340.

[4] D. F. Morris and F. Basolo, *J. Amer. Chem. Soc.*, 1968, **90**, 2531, 2536.

[5] F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, 1969, **8**, 696.

[6] A. B. Callear, *Endeavour*, 1967, **26**, 9; J. M. Kelly, H. Hermann, and E. Korner von Gustorf, *J.C.S. Chem. Comm.*, 1973, 105.

[7] J. S. Ogden and J. J. Turner, *Chem. in Britain*, 1971, **7**, 186.

[8] O. Crichton and A. J. Rest, *J.C.S. Dalton*, 1977, 536.

[9] O. Crichton and A. J. Rest, *Proc. 6th Internat. Conf. Organometallic Chem.*, Amherst, Massachusetts, 1973.

[10] R. B. King, *Organometallic Synth.*, 1965, **1**, 167.

and AnalaR Ni[SO_4] in water with cut-on and cut-off points adjusted by dilution]. Additionally, because of the extreme sensitivity of some of the primary photoproducts (see below) to visible light, it was necessary to remove any visible light from the radiation emitted by the Nernst filament of the i.r. spectrometer. This was achieved using a germanium interference filter (Ocli Optical Coatings).[8]

RESULTS AND DISCUSSION

Photolysis of [$Fe(CO)_2(NO)_2$] *in Argon and Methane Matrices.*—Infrared spectra from an experiment with [$Fe(CO)_2(NO)_2$] in argon, using the germanium filter, are shown in Figure 1. At high dilution (1 : 10 000), the spectrum of the parent complex [Figure 1(*a*)] consisted of four strong bands corresponding to the two terminal carbonyl and two terminal nitrosyl modes expected for C_{2v} symmetry. As with [$Co(CO)_3(NO)$], higher resolution spectra show that, with the possible exception of the highest-frequency absorption, A_1[ν(CO)], each band is split * (Table 1).

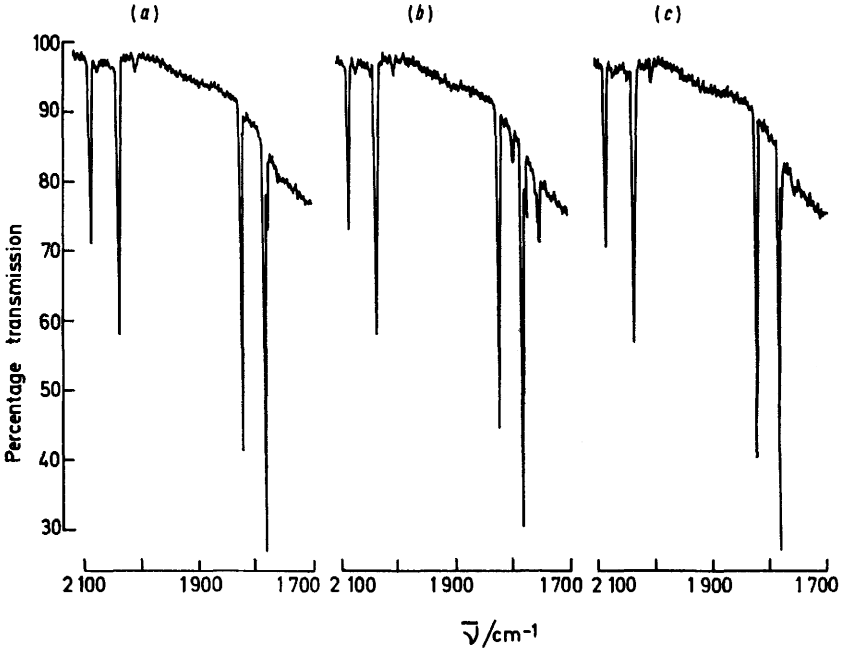

FIGURE 1 Infrared spectra from an experiment with [$Fe(CO)_2(NO)_2$] isolated in an argon matrix: (*a*) after deposition; (*b*) after 10-min photolysis with u.v. light (filter A); and (*c*) after photolysis for another 5 min with visible light (filter B)

On u.v. photolysis with a filtered medium-pressure mercury arc (filter A) new bands appeared [Figure 1(*b*)]. Removal of the Nernst filter or exposure to visible light (filter B) rapidly regenerated the original spectrum [Figure 1(*c*)]. No other new bands of significant intensity could be produced by photolysis with light of different wavelengths. From the position of the two new bands produced in this experiment (doublets at 1 796 and 1 794 cm^{-1} and 1 750 and 1 747 cm^{-1}), it is evident that they are both nitrosyl vibrations. The ratio of the intensities of these two bands was *ca.* 1 : 3 ($I_{1795} : I_{1750}$), so that it is probable that they arise from a planar [$Fe(CO)(NO)_2$] fragment even though no carbonyl vibration is visible.† A simple Cotton–Kraihanzel-type force-constant calculation [12] readily explains the difficulty in observing the terminal carbonyl band. If it is assumed that loss of a CO ligand from [$Fe(CO)_2(NO)_2$] causes the same percentage change in k_{CO} as is observed on going from [$Co(CO)_3(NO)$] to [$Co(CO)_2(NO)$], the position of ν(CO) for [$Fe(CO)_2(NO)_2$] is calculated to be 2 043 cm^{-1}. A band close to this wavenumber, especially since it would be weak because of low conversion of parent into primary photoproduct, might well be obscured by the strong parent absorption at 2 041 cm^{-1}.

TABLE 1

Positions (cm^{-1}) of bands appearing in experiments with [$Fe(CO)_2(NO)_2$] isolated in argon and methane matrices

	[$Fe(CO)_2(NO)_2$]			[$Fe(CO)(NO)_2$]	
	Argon	Methane		Argon [a]	Methane [a]
A_1[ν(CO)]	2 089	2 087	A_1[ν(CO)]	2 043 [b]	2 034 [c]
B_1[ν(CO)]	2 041 2 038	2 039	A_1[ν(NO)]	1 796 1 794	1 792 1 787 [c]
A_1[ν(NO)]	1 820 1 817	1 815	B_1[ν(NO)]	1 750 1 747	1 747 1 741 [c]
B_2[ν(NO)]	1 779 1 775	1 774			

[a] Additional weak bands were observed during photolysis in argon (at 2 051 cm^{-1}) and methane (at 2 072, 2 044, 1 942, 1 783, and 1 723 cm^{-1}) matrices (see text). [b] Calculated value. [c] These bands may be the 2*A*′ and *A*″ modes of the complex [$Fe(CO)(NO)_2$] · · · CH_4.

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* The splittings for the series [$M(CO)_{4-x}(NO)_x$] will be discussed in detail elsewhere.[11]

† In some experiments a weak band did appear at 2 051 cm^{-1}, but since it was unaffected by the Nernst radiation and visible light it is not related to the nitrosyl vibrations.

[11] O. Crichton and A. J. Rest, unpublished work.

[12] L. M. Haines and M. M. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 53.

A corresponding experiment in a methane matrix is illustrated in Figure 2. As observed for [Co(CO)$_3$(NO)], the spectrum of [Fe(CO)$_2$(NO)] in methane [Figure 2(*a*)] was slightly different from that in argon in respect of a slight matrix shift (up to 5 cm^{-1} to lower wavenumbers) and smaller splittings (Table 1). The very weak bands marked (5) are due to a small amount of [Fe(CO)$_5$] present in the [Fe(CO)$_2$(NO)$_2$] sample. As in argon, u.v. photolysis (filter A) caused two new nitrosyl vibrations to appear [Figure 2(*b*)]. Both these bands consisted of two fairly well spaced components, a weaker one at higher wavenumbers and a stronger one at lower wavenumbers ($I_{1792} < I_{1787}$ and $L_{1747} < I_{1741}$). In addition to these nitrosyl bands, a new very weak band appeared at 1 942 cm^{-1} and the lower parent carbonyl vibration became significantly broadened to lower wavenumbers. Changes also occurred in the [Fe(CO)$_5$] impurity bands owing to the photochemical production of [Fe(CO)$_4$].[13,14] Photolysis with visible light (filter B) resulted in a spectrum [Figure 2(*c*)] which is virtually identical with the one obtained before photolysis.

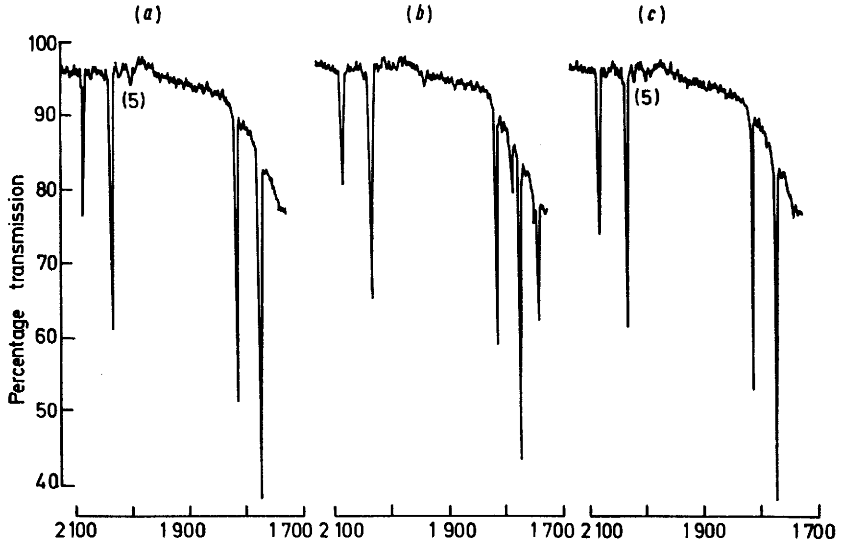

FIGURE 2 Infrared spectra from an experiment with [Fe(CO)$_2$(NO)$_2$] isolated in a methane matrix: (*a*) after deposition; (*b*) after 90-s u.v. photolysis (filter A); and (*c*) after photolysis for another 2 min with visible light (filter B)

More spectra from the same methane-matrix experiment are shown in Figure 3. Repeated cycles of brief forward photolysis followed by long-wavelength reversal produced no overall change in the spectra [Figure 3(*a*)], demonstrating that the reaction is essentially completely reversible. Forward photolysis can also be promoted with long-wavelength u.v. and violet radiation (filter C). Comparison of the spectra in Figures 2(*b*) and 3(*b*) shows that, although similar, the effects of filters A and C are different. Photolysis with filter C [Figure 3(*b*)] resulted in lower overall conversion and an increase in the intensities of the two higher-wavenumber components of the nitrosyl vibrations relative to the lower wavenumber components (*i.e.* $I_{1792} \gg I_{1787}$ and $I_{1747} \gg I_{1741}$). Practically none of the minor product [ν(NO) at 1 787 and 1 741 cm^{-1}] was formed. Prolonged exposure to the unfiltered mercury arc resulted in the spectrum shown in Figure 3(*c*). The total amount of product present at this stage was greater than any previous stage and a new terminal-carbonyl vibration (2 034 cm^{-1}) was clearly resolved from the lower band of the parent complex (2 039 cm^{-1}). Although the total intensity of the product nitrosyl vibrations increased greatly, the higher-frequency components of the two bands (1 792 and 1 747 cm^{-1}) were virtually absent. In addition to the weak band at 1 942 cm^{-1}, which also appeared previously, other unassigned weak bands were present at 2 072, 2 044, 1 783, and 1 723 cm^{-1}. At this stage in the experiment most of the changes which have occurred cannot be reversed by long-wavelength irradiation (filter B).

The three strongest bands in the final spectrum are fairly close to the bands previously assigned to [Fe(CO)(NO)$_2$] in the argon experiment (Table 1). The disturbing feature of this assignment is that both nitrosyl bands consist of two components whose relative intensities depend on the photolysis source. In view of the small splitting of the nitrosyl bands of the parent complex in the original spectrum (Table 1), it is possible that two different [Fe(CO)(NO)$_2$] product species are involved, although it is perhaps doubtful whether there is a fundamental difference. Possibly one of the species present is actually [Fe(CO)(NO)$_2$] $\cdots$ CH$_4$ similar to the [Fe(CO)$_4$] $\cdots$ CH$_4$ species described by Poliakoff and

[13] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1973, 1351.
[14] M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1974, 2276.

Turner.[14] Interestingly, the intensity ratio of the nitrosyl bands present in Figure 3(*c*) (*i.e.* $I_{1787} : I_{1741}$) is substantially less than 1 : 3, suggesting that the species responsible for them is significantly non-planar. Assignment of this species as a weak $[Fe(CO)(NO)_2] \cdots CH_4$ complex might also explain why the terminal-carbonyl absorption is shifted far enough away from the lower band of $[Fe(CO)_2(NO)_2]$ to be clearly resolved.

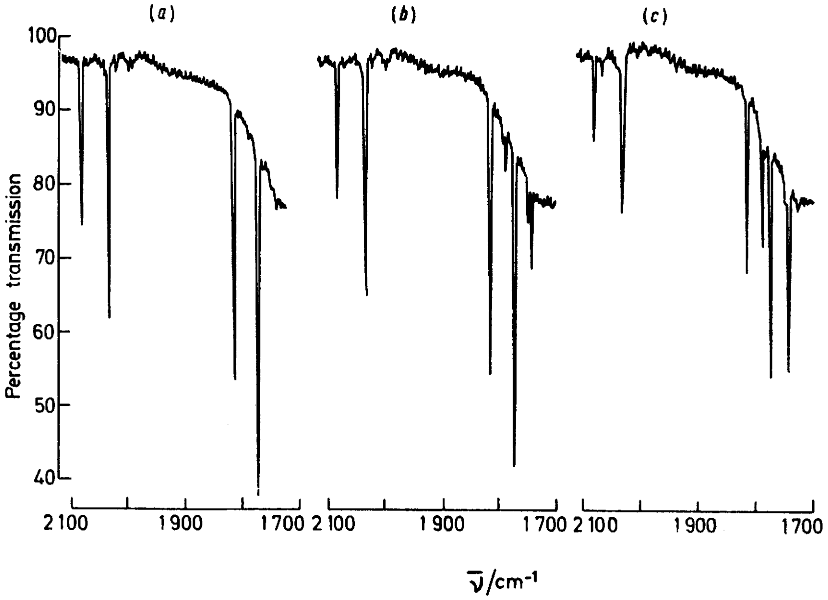

FIGURE 3 Further spectra from the experiment illustrated in Figure 2: (*a*) after several cycles of forward and reverse photolysis (filters A and B); (*b*) after photolysis for another 5 min with u.v. and visible radiation (filter C); and (*c*) after photolysis for another 30 min with the unfiltered mercury arc

The irreversibility of the processes leading to the appearance of weak bands in the final stage of the experiment in methane [Figure 3(*c*)] makes assignment of them very difficult. Protracted mercury-arc photolysis of a matrix can cause some diffusion of molecular fragments to produce polynuclear aggregates which typically possess weak, rather broad, bands at relatively high wavenumbers,[15] and conceivably the bands at 2 072 and 2 044 cm^{-1} are carbonyl absorptions of such aggregates.

Photolysis of $[Fe(CO)_2(NO)_2]$ *in Nitrogen Matrices.*†—In a pure nitrogen matrix all the four high-wavenumber i.r.-active fundamentals of $[Fe(CO)_2(NO)_2]$ showed fine splittings. The lower-wavenumber terminal-carbonyl and both nitrosyl absorptions are obviously at least doublets even under low resolution [Figure 4(*a*)]. Under better resolution, the upper A_1 carbonyl band, which could not be resolved in argon or methane, appeared as a doublet (2 090 and 2 086 cm^{-1}) while the other bands showed signs of further splittings (Table 2).

Brief photolysis with u.v. light (filter A) produced five new absorptions [bands (1)—(5)] in addition to a weak band due to liberated CO at 2 139 cm^{-1} [Figure 4(*b*)]. In view of the splitting of all the five product bands, it is not immediately clear how many fundamentals are involved. Comparison of the spacing and relative intensity of the parent nitrosyl absorptions with the four product nitrosyl bands [(2)—(5) in Figure 4(*b*)] suggests that they form two pairs [(2) and (4), (3) and (5)], corresponding to two distinct dinitrosyl species. Exposure to visible light (filter B) caused all the product bands to decrease in intensity, while the absorptions of the parent complex grew [Figure 4(*c*)]. Careful monitoring of the intensities of the product bands showed that during long-wavelength photolysis the weaker pair of product nitrosyl bands [(3) and (5)] decreased in intensity proportionately more than the stronger pair [(2) and (4)] and the product carbonyl vibration [(1)].

TABLE 2

Positions (cm^{-1}) of bands observed in experiments with $[Fe(CO)_2(NO)_2]$ in pure nitrogen matrices

$[Fe(CO)_2(NO)_2]$		$[Fe(CO)(N_2)(NO)_2]$		$[Fe(N_2)_2(NO)_2]$	
$A_1[\nu(CO)]$	2 090 2 081	$A'[\nu(NN)]$	2 270 [a] 2 268 [b] 2 262	$A_1[\nu(NN)]$	2 256
$B_1[\nu(CO)]$	2 042 2 038	$A_1[\nu(CO)]$	2 054 [a] 2 050 [b] 2 048	$B_1[\nu(NN)]$	2 241
$A_1[\nu(NO)]$	1 819 1 815	$A'[\nu(NO)]$	1 806 1 804	$A_1[\nu(NO)]$	1 795 1 792
$B_2[\nu(NO)]$	1 777 1 775	$A''[\nu(NO)]$	1 762 1 760	$B_2[\nu(NO)]$	1 750 1 748

[a] Band became more intense on annealing. [b] Band became less intense on annealing.

In experiments in which a larger quantity of $[Fe(CO)_2(NO)_2]$ was initially present, very weak i.r. bands appeared in the 2 150—2 300 cm^{-1} region during u.v. photolysis (filter A). One of these bands, a triplet at

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† The germanium disk filter was not used for experiments in N_2 matrices.

[15] M. A. Graham, Ph.D. Thesis, Cambridge University, 1971.

2 270, 2 268, and 2 262 cm^{-1}, appeared to behave similarly to bands (1), (2), and (4) in the lower-wavenumber region of the i.r. spectrum.

Further spectra from the experiment illustrated in Figure 4 are shown in Figure 5. More prolonged u.v. photolysis using a different filter (filter D) produced the spectrum shown in Figure 5(*a*). Slightly more of the major product was present than in Figure 4(*b*) and a

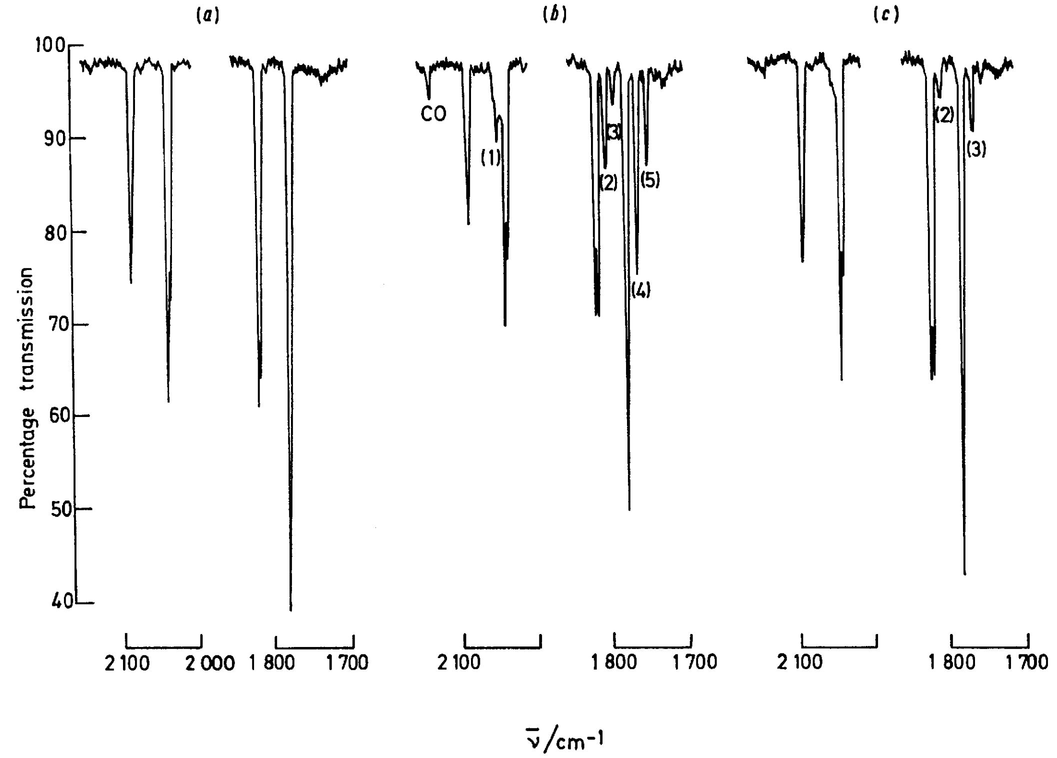


FIGURE 4 Infrared spectra from an experiment with [Fe(CO)$_2$(NO)$_2$] isolated in a nitrogen matrix: (*a*) after deposition; (*b*) after 1-min photolysis with u.v. light (filter A); and (*c*) after photolysis for another 5 min with visible light (filter B)

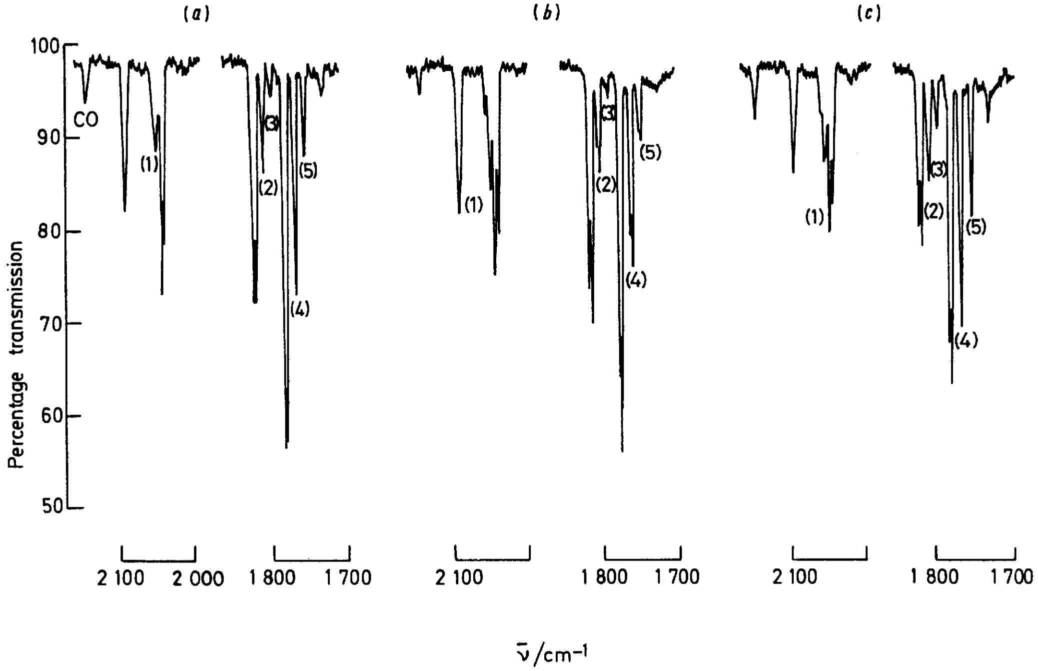
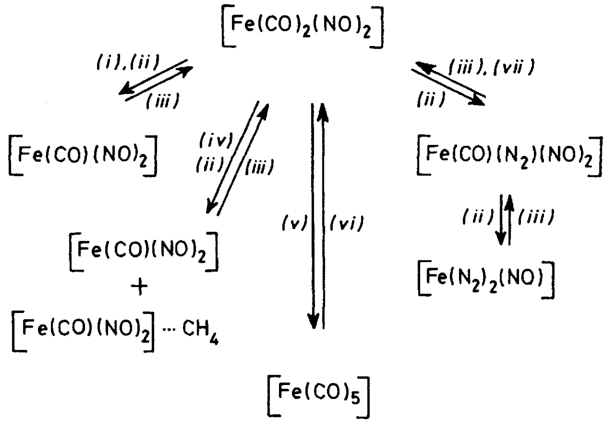


FIGURE 5 Further spectra from the experiment illustrated in Figure 4: (*a*) after 5-min photolysis with u.v. light (filter D); (*b*) after annealing the matrix; and (*c*) after photolysis for another 5 min with the unfiltered mercury arc

completely new band appeared at 1 724 cm^{-1}. Annealing the matrix, *i.e.* increasing the temperature of the matrix briefly to 30—35 K by exerting a ' back pressure ' on the liquid-hydrogen coolant and then cooling the matrix to 20 K before running a spectrum, at this stage [Figure 5(*b*)] caused a general ' sharpening-up ' of all the bands except for that at 1 724 cm^{-1} which disappeared. The species responsible for the band at 1 724 cm^{-1} must therefore presumably be a co-ordinatively unsaturated fragment, *cf.* the reaction of [Ni(CO)$_3$] with CO at 30 K.[16] The final spectrum [Figure 5(*c*)] shows the effect of photolysing the annealed sample with the unfiltered mercury arc. Rather more of all the product species was present at this stage of the experiment than previously and the appearance of the products was no longer completely reversed by irradiation with visible light [see Figure 4(*c*)]. A further interesting feature of the spectrum [Figure 5(*c*)] is that the effect of annealing on the splitting patterns of the various bands was reversed by exposure to white light.

The major product formed from [Fe(CO)$_2$(NO)$_2$] in nitrogen matrices must be [Fe(CO)(N$_2$)(NO)$_2$] since, in addition to a dinitrogen absorption (at 2 270, 2 268, and 2 262 cm^{-1}), it possesses a carbonyl band (at 2 054, 2 050, and 2 048 cm^{-1}) and two nitrosyl bands (at 1 806 and 1 804 cm^{-1}, 1 762 and 1 760 cm^{-1}) (Table 2). The product responsible for the second pair of nitrosyl bands [(3) and (5); 1 795 and 1 792, 1 750 and 1 748 cm^{-1} respectively] must also be a dinitrosyl complex and the possible candidates are the saturated molecule [Fe(N$_2$)$_2$(NO)$_2$] and the two unsaturated fragments [Fe(N$_2$)(NO)$_2$] and [Fe(CO)(NO)$_2$]. Since the product is completely stable to radiation from the Nernst source, it is extremely unlikely that the product is [Fe(CO)(NO)$_2$] because this fragment is reactive under Nernst irradiation (see above). The complex [Fe(N$_2$)(NO)$_2$] might also be expected to react with CO in the absence of the Nernst filter. A further argument against assigning the minor product as [Fe(N$_2$)(NO)$_2$] is the similarity of the positions of the nitrosyl absorptions to those of [Fe(CO)(NO)$_2$]. Replacement of CO in [Fe(CO)(NO)$_2$] by N$_2$ should cause a significant shift of the nitrosyl bands to lower wavenumbers {*cf.* [Fe(CO)$_2$(NO)$_2$] and [Fe(CO)(N$_2$)(NO)$_2$] in Table 2}. The most likely identity for the minor product is thus, by elimination, [Fe(N$_2$)$_2$(NO)$_2$)]. Although no corresponding N–N stretching modes can be unambiguously assigned, because of the weakness of the bands, two weak bands were observed at 2 256 and 2 241 cm^{-1}, in addition to the band of [Fe(CO)(N$_2$)(NO)$_2$] at *ca.* 2 268 cm^{-1}, in experiments where large amounts of both major and minor species were produced. N–N Stretching bands for [Ni(CO)$_2$(N$_2$)$_2$], which is isostructural with [Fe(N$_2$)$_2$(NO)$_2$], have been observed[17] at 2 270 and 2 240 cm^{-1}. Further confirmatory evidence for assigning the minor product as [Fe(N$_2$)$_2$(NO)$_2$] comes from a comparison of the fine structure of the nitrosyl absorption of [Fe(CO)$_2$(NO)$_2$] and the two products in N$_2$ matrices. Particularly after annealing, there is a pronounced resemblance between the splittings observed in each of the three pairs of nitrosyl bands. It seems reasonable to suppose, therefore, that these three pairs of bands arise from the series of isostructural species [Fe(CO)$_2$(NO)$_2$], [Fe(CO)(N$_2$)(NO)$_2$], and [Fe(N$_2$)(NO)$_2$].

Mechanism.—The reactions of [Fe(CO)$_2$(NO)$_2$] in argon and methane matrices show that CO ejection can take place to give a co-ordinatively unsaturated species [Fe(CO)(NO)$_2$] as a primary photolysis product with the additional possibility for methane of forming a weak complex [Fe(CO)(NO)$_2$]$\cdots$CH$_4$. The reactivity of [Fe(CO)(NO)$_2$] is demonstrated both by the recombination with CO when the matrix is irradiated with light of a longer wavelength and by the reaction with N$_2$ to give [Fe(CO)(N$_2$)(NO)$_2$]. No evidence was obtained in this study for NO ejection, but in a separate study the photolysis of [Fe(CO)$_2$(NO)$_2$] in a CO matrix gave [Fe(CO)$_5$].[18] The reactions of [Fe(CO)$_2$(NO)$_2$] in matrices are summarised in Scheme 2.



SCHEME 2 (*i*) Argon; (*ii*) $h\nu$; (*iii*) $h\nu'$; (*iv*) CH$_4$; (*v*) CO,$h\nu''$; (*vi*) NO–Ar, $h\nu'''$; (*vii*) N$_2$

The isolation of [Fe(CO)(NO)$_2$] in argon and methane matrices gives strong support to the species (A) in Scheme 1 but no evidence for a counterpart to (B) could be found. Perhaps the failure to observe such a species as (B) in a matrix results from an unfavourable overlap of bands in the u.v.–visible spectrum so that no selective photolysis source could be found to promote its formation. A similar situation is found for [Fe(CO)$_2$(NO)$_2$] in a CO matrix where, despite replacement of an NO ligand, only [Fe(CO)$_5$] is observed and no bands could be found for a mononitrosyl species.[18]

We thank the S.R.C. together with I.C.I. Ltd., Petrochemicals Division, Billingham, for the award of a C.A.P.S. Studentship (to O. C.), and the Royal Society for the award of a Pickering Research Fellowship (to A. J. R.).

[6/1353 *Received*, 12*th July*, 1976]

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[18] O. Crichton, M. Poliakoff, A. J. Rest, and J. J. Turner, *J.C.S. Dalton*, 1973, 1321.